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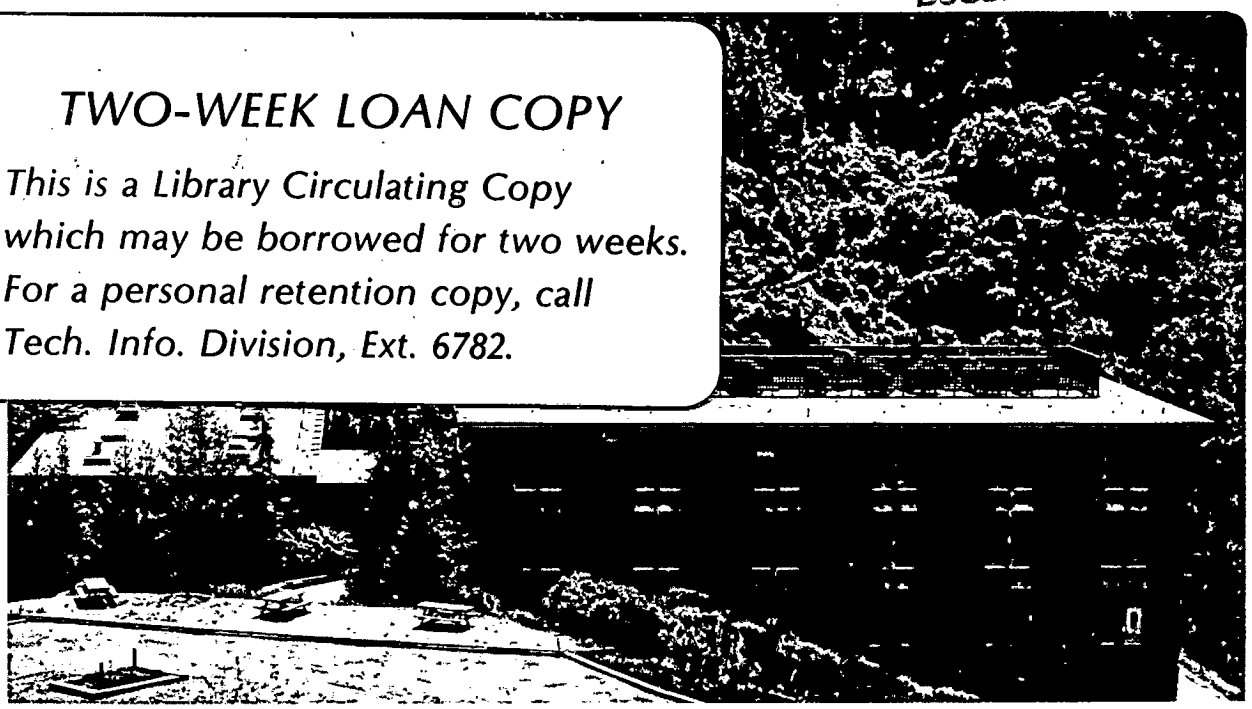

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ABSTRACT

Anomalous scattering terms f' and f'' for Pr and Sm were derived from diffraction experiments with synchrotron radiation and crystals of $NaPrEDTA \cdot 8H_2O$ and $NaSmEDTA \cdot 8H_2O$ at wavelengths near the L_3 absorption edges. Changes in f' ranging from -7 to -26 e for Pr and from -6 to -21 e for Sm, and f'' values up to 28 e for Pr and 23 e for Sm occur at wavelengths within 0.003 Å of the L_3 edges. These large effects can be used to solve the phase problem for macromolecular crystallography by diffraction measurements with one crystal at two or more wavelengths. It is estimated that one atom of praseodymium in a molecule of 800,000 daltons could be enough.

L_3-Edge Anomalous Scattering of X-rays by Praseodymium and Samarium

Sir:

We report measurements of the anomalous scattering of X-rays by atoms of praseodymium and samarium at wavelengths through their L_3 absorption edges. Values of both f' and f'', the real and imaginary components of the anomalous scattering, were derived from diffraction experiments using synchrotron radiation. Both components exhibit exceptionally large changes in a narrow interval of wavelength, changes which offer a powerful tool for solving the phase problem in crystal structure analysis.

Synchrotron radiation provides a continuous X-ray spectrum intense enough for single-crystal diffraction experiments at arbitrary wavelengths selected by a narrow-bandpass crystal monochromator. Experiments with cesium hydrogen tartrate[1,2] showed that f' for cesium dips to -26.7 ± 0.3 electrons and f'' rises to 16.1 ± 0.8 electrons near the L_3 edge (2.474 Å). These effects are large enough to be useful in solving macromolecular crystal structures, but cesium is not very convenient for this purpose because of strong absorption of X-rays by light atoms at this wavelength. The rare earth elements have L_3 edges (2.26 Å for lanthanum to 1.34 Å for lutetium) which span the wavelength range normally used to study large molecules. X-ray absorption spectra[3] for several rare earth compounds show sharp and intense lines at the respective L_3 edges, indicating anomalous scattering effects as large or larger than those for cesium. This indication is confirmed by the present results.

The method[4] is to use least-squares adjustment to derive f', f'' and a scale factor from diffraction intensities measured at the wavelength of interest with a crystal whose structure is known from a conventional experiment at another wavelength. We used crystals of sodium praseodymium ethylenediaminetetraacetate octahydrate ($NaPrC_{10}H_{12}N_2O_8 \cdot 8H_2O$) and the isomorphous samarium salt which, like the same salts of most of the other rare earth elements, crystallize in the non-centric space group Fdd2.[5-7] The atomic coordinates and thermal parameters were determined using Mo Kα radiation.[8] In one praseodymium experiment we measured 970 reflections (without any repetitions) in the range $0.08 < \lambda^{-1}\sin\theta < 0.42$. At each other wavelength we measured 48 reflections in the range of $\lambda^{-1}\sin\theta$ from 0.37 to 0.41, including 23 Bijvoet pairs and two centric reflections, from one to three times each. One reflection was repeated after each 10 or 12 measurements to serve as an intensity standard. Subsequent study of the standard-reflection profiles indicate changes in wavelength during some of the praseodymium experiments, probably caused by movement of the electron orbits in the storage ring. Corrections as large as 0.0011 Å based on the observed changes in Bragg angle are included in the wavelengths listed in Table 1. Absorption corrections were calculated by analytical integration[9] with the crystal shapes described by 9 or 10 plane faces and absorption coefficients ranging from 100 to 460 cm^{-1}. Other details of the method and apparatus are described elsewhere.[1,2,10,11]

The values found for the anomalous scattering terms are plotted in Fig. 1 and listed, with the respective R values for each data set, in Tables 1 and 2. For both elements, f'' exhibits the striking resonance line which is observed in the absorption curves. The peak values are substantially larger than we observed for cesium, and in the praseodymium case more than double the values for any element near K or L edges calculated by Cromer and Liberman[12] with a model which neglects fine structure lines.

The curves for f' show the characteristic shape demanded by the dispersion relation for a sharp absorption line. In Fig. 1 the broken lines show f' calculated from f'' by a Kramers-Kronig integration;[2] for this purpose the experimental f'' curve was extended to higher and lower wavelengths by estimated values. Errors in these estimates affect the calculated curve by an additive constant, but contribute little to its shape in this narrow wavelength interval. The agreement of the curves is excellent.

The wavelength spread of the X-ray beam from the monochromator, estimated as $\Delta\lambda/\lambda = 10^{-3}$, is comparable to the widths observed for the peaks in f' and f''. Thus it may be that even larger variations can be observed with more nearly monochromatic X-rays. We intend to test this possibility.

The use of f'' to help solve the phase problem in X-ray crystallography, by means of the intensity difference it causes for reflections hkl and $\bar{h}\bar{k}\bar{l}$, is well established. Larger values of f''

make the method more powerful. The effect of a change in f' is similar to that of a change in atomic number. Thus experiments at two or more wavelengths where f' is different can be analyzed like isomorphous replacement data. Again the utility of the method is sensitive to the magnitude of the changes in f'. Large anomalous scattering terms also facilitate the determination of heavy atom positions. Once the positions are known for the anomalously scattering atoms, one can derive phase angles without ambiguity from diffraction data measured for one crystal at three or more wavelengths, or at two or more wavelengths if both members of each Bijvoet pair are measured. Mathematical procedures for this method have been described by Hoppe and Jakubowski.[13] They showed that phases could be determined with an accuracy of about 50° for many of the reflections of a protein (erythrocruorin, M.W. ~16,000) using two wavelengths near the K edge of iron, where the anomalous scattering effects are about 7 times smaller than those reported here for praseodymium. An atom of praseodymium in a molecule of 800,000 daltons would be a somewhat similar case, since according to Wilson statistics the percentage effects of anomalous scattering depend on the ratio of changes in f to the square root of the number of atoms.[14]

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Table 1. Praseodimium Anomalous Scattering.

λ(Å)	f'	f''	R[a]
2.0833	-18.5(6)	4.3(6)	0.045
2.0817	-21.6(5)	5.1(4)	0.050
2.0810	-22.8(5)	5.4(4)	0.077
2.0805	-25.0(7)	7.9(6)	0.083
2.0796	-25.7(6)	8.1(4)	0.068
2.0790	-26.5(3)	19.7(2)	0.084[b]
2.0788	-25.8(11)	22.3(9)	0.056
2.0784	-24.0(13)	25.6(11)	0.053
2.0776	-17.2(13)	27.8(11)	0.041
2.0772	-14.8(12)	26.9(11)	0.038
2.0767	-6.6(10)	18.7(13)	0.036
2.0745	-10.3(7)	10.5(9)	0.036

[a] $R = \Sigma|\Delta F|/\Sigma|F_o|$.

[b] 970 reflections.

Table 2. Samarium Anomalous Scattering.

λ(Å)	f'	f''	R
1.8512	-15.6(5)	4.1(6)	0.035
1.8490	-17.2(5)	4.5(5)	0.037
1.8479	-18.6(5)	6.5(5)	0.057
1.8468	-21.3(10)	7.7(10)	0.082
1.8463	-19.5(10)	14.0(13)	0.072
1.8457	-18.6(8)	22.0(7)	0.033
1.8452	-8.5(16)	23.3(18)	0.050
1.8441	-6.3(18)	14.0(24)	0.078
1.8425	-10.0(9)	9.9(12)	0.047
1.8397	-12.7(10)	10.7(12)	0.042

FIGURE CAPTION

Fig. 1. Anomalous scattering terms f' and f'' near the L_3 edges for samarium (left) and praseodymium (right). The broken lines are calculated from f'' by a dispersion relation.

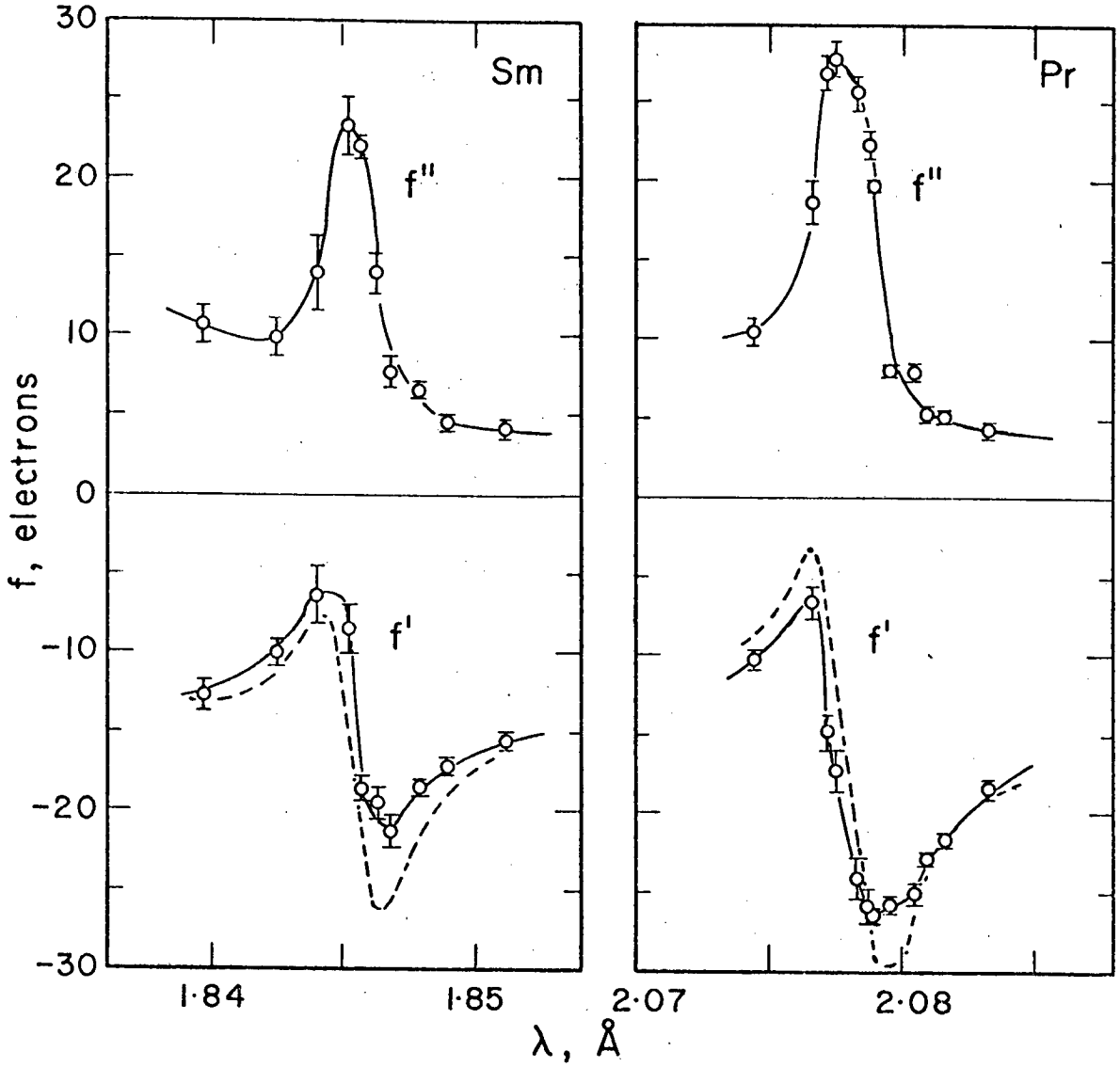

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Fig. 1

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